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(54) Removal of acid gases from a gas mixture

(57) Acid gases e.g. H_2S, CO_2, COS, are removed from a gas mixture by contacting at elevated pressure with an aqueous solution of a dialkyl - mono - alkanolamine (in particular diethyl - mono - ethanolamine), which aqueous solution does not contain a sterically hindered amine, i.e. a compound containing a secondary amine group bonded to a secondary or tertiary carbon atom, or a primary amine group bonded to a tertiary carbon atom. A physical solvent (e.g., sulfolane) may be present in the aqueous solution. The gas mixture may be natural gas, a gas obtained by the gasification of petroleum or coal, or a gas obtained by conversion of carbon monoxide and water into carbon dioxide and hydrogen.

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SPECIFICATION

A process for the removal of acid gases from a gas mixture

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The invention relates to a process for the removal of acid gases from a gas mixture.

For many years aqueous solutions of alkanolamines have been used as absorbents for the
10 removal of acid gases (by which are meant in this application hydrogen sulphide and carbon dioxide and also compounds which can readily be converted thereinto, such as carbon oxysulphide) from liquids, for example hydrocarbon mixtures and in particular
15 from gases which are at elevated pressure, such as natural gas, refinery gases. These solutions are suitable to reduce to lower values the acid gas contents of the gases or liquids to be purified.

The reduction of the content of acid gases, in par-
20 ticular H_2S, to a minimum is becoming increasingly important on account of demands made by the authorities in connection with environmental hygiene.

The gases to be purified are generally contacted
25 with the absorbent at elevated pressure in an absorption column, with the result that the absorbent becomes loaded with acid gases. The regeneration of the loaded absorbent (i.e., the removal of all or the greater part of the absorbed gases therefrom) gene-
30 rally occurs by heating it with steam in a regeneration column. Since steam (i.e., the energy to prepare steam) is expensive, the aim will be to keep the quantity of loaded absorbent as small as possible. It will be clear that on the one hand the aim is to use
35 absorbents having a high acid gas loading capacity and on the other hand, if one intends to remove in particular H_2S from CO_2-containing gas mixtures, to use absorbents which enable H_2S to be removed selectively with respect to CO_2 from gas mixtures.
40 The use of the smallest possible quantity of loaded absorbent to be regenerated is not only favourable to steam consumption, but the absorbent circulation system can also be constructed smaller than in the case of absorbents having a lower loading capacity
45 and/or selectivity.

A type of alkanolamines has now been found of which the aqueous solutions are selective to H_2S with respect to the absorption of H_2S from gas mixtures also containing CO_2 and also have a large
50 capacity for absorbing acid gases.

The invention therefore relates to a process for the removal of acid gases from a gas mixture, characterized in that said gas mixture is contacted at elevated pressure with an aqueous solution of a dialkyl -
55 mono - alkanolamine, which aqueous solution does not contain a sterically hindered amine.

By elevated pressure is meant a pressure of at least 2 bar. Preferably, the pressure is at least 5, in particular at least 10 bar.
60 By aqueous solution is meant a solution which contains at least 5% by weight of water.

A sterically hindered amine is defined as a compound which contains either a secondary amine group bound to a secondary or a tertiary carbon
65 atom, or a primary amine group bound to a tertiary

carbon atom.

The two alkyl groups in the dialkyl - mono - alkanolamine need not be the same; methyl, ethyl, propyl and isopropyl groups are very suitable.
70 As very suitable alkanol groups may be mentioned the ethanol, propanol and isopropanol group.

Diethyl - mono - ethanolamine is preferred as dialkyl - mono - alkanolamine.

Generally, at least 10% by weight of the aqueous
75 solution consists of dialkyl - mono - alkanolamine; this percentage is preferably between 15 and 60.

If one intends to remove H_2S selectively from gas mixtures containing CO_2 it is advantageous to use an absorption column which contains a relatively small
80 number of trays, while the gas velocity will be chosen relatively high.

It is usual to contact the gas to be treated and the absorbent – in the present case the dialkyl - mono - alkanolamine solution – countercurrently with each
85 other in a tray column. The treated gas then leaves the vertical column near or at the top thereof, and the loaded absorbent, which contains the absorbed hydrogen sulphide and carbon dioxide, leaves said column near or at its bottom. Tray columns usually
90 contain valve trays, bubble cap trays or perforated sheets. Other types of trays or sheets may also be used. It is also possible to use packed columns. The gas to be treated is preferably contacted with the absorbent at temperatures below 80°C, in particular
95 between 15 and 50°C.

The regeneration of the loaded aqueous solution of a dialkyl - mono - alkanolamine is suitably carried out in a regeneration column by heating the loaded absorbent and/or stripping it with an inert gas, such
100 as, for example, steam, preferably at temperatures of 80-120°C. Consequently, a gas containing H_2S, CO_2 and other components, if any, is separated from the loaded absorbent and a regenerated absorbent is obtained. The solution to be regenerated can very
105 suitably be heated by means of indirect heating with low-pressure steam. It is also possible to use direct injection of steam.

The aqueous solutions of dialkyl - mono - alkanolamines according to the invention have a large
110 capacity for the absorption of acid gases and are therefore also very suitable for the non-selective removal of CO_2 from gas mixtures at elevated pressure, since as a result of the relatively large quantity of CO_2 which can be absorbed, the quantity of abso-
115 rbent to be used and consequently the quantity of heat (usually steam) required for the regeneration of the loaded absorbent are smaller than when using amines with a lower capacity. For such removal of CO_2 it is of advantage that a physical solvent for acid
120 gases is also present in the aqueous solution of the dialkyl - mono - alkanolamine, since as a result thereof the capacity for absorption and/or the rate of absorption of the absorbent is further increased, foam formation is inhibited and any volatile mercap-
125 tans present in the gases to be purified are removed therefrom. Moreover, the steam consumption per volume unit of solvent to be regenerated is also favourably affected.

As physical solvents are very suitable N-methyl
130 pyrrolidone, propylene carbonate, methanol and in

particular tetrahydrothiophene dioxide (sulfolane).
The quantity of physical solvent may vary between
wide limits and may very suitably be 10-40% by
weight of the aqueous solution.

5   The process according to the invention is very suitable to be used for the removal of CO_2 and/or H_2S
and/or COS from natural gas, from gases obtained
by the gasification of petroleum or coal, and from
gases obtained by converting CO with H_2O into CO_2
10   and H_2.

EXAMPLE 1

A gas obtained in the gasification of coal (composition 37.1% by vol. of CO_2, 0.41% by vol. of H_2S, balance H_2) was treated countercurrently with an aque-
15   ous 2-molar solution of diethyl mono-ethanolamine
(DEMEA) (according to the invention), and diisopropanolamine (DIPA) and methyl diethanolamine
(MDEA) (both not according to the invention),
respectively, in a tray column containing 55 trays at a
20   pressure of 33 bar and a temperature of 40°C. The
gas velocity was 20 cm/sec. The mutual ratio of the
required volumes of the aqueous solutions of the
amines in order to obtain a purified gas containing
less than 4% by volume of CO_2 and less than 10
25   ppmv of H_2S was determined. It was found that if the
volume required of the DEMEA-containing solution
was assumed to be 1, the volume required of the
MDEA- and DIPA- containing solutions was 1.59 and
2.86 respectively. In the process according to the
30   invention the volume of aqueous amine solution to
be used is therefore much smaller than in the known
processes, so that the quantity of aqueous amine
solution to be regenerated and recycled is much
smaller than in known processes.

35   ### EXAMPLE 2

A gas mainly consisting of methane, which contained as contaminants 1.6% by vol. of CO_2 and 30
ppmv of H_2S, was treated countercurrently with
absorbents containing 35 parts by weight of water,
40   15 parts by weight of sulfolane and 50 parts by
weight of DEMEA, MDEA and DIPA, respectively, in
an absorption column with 6 trays at a pressure of 80
bar and a gas velocity of 40 cm/sec. The mutual ratio
of the required volumes of absorbent in order to
45   obtain a gas having an H_2S-content of less than 3
ppmv of H_2S was determined, and the removed
amount of CO_2 present in the starting gas was calculated. The table below shows that the required volume of the DEMEA-containing absorbent (according
50   to the invention) is the smallest, while moreover the
selectivity of this absorbent to H_2S removal in relation to CO_2 removal is higher than that of the DIPA-
containing absorbent.

TABLE

Amine in absorbent	Required quantity of absorbent	CO_2 absorbed in absorbent (% on quantity of CO_2 in starting gas)
DEMEA	1	20.2
MDEA	1.43	20.1
DIPA	1.79	40.1

EXAMPLE 3

55   In order to purify a gas that mainly consisted of
CH_4 and contained as contaminants 10% of CO_2, 8%
of H_2S and 100 ppmv of CH_3SH, this gas was treated
countercurrently (gas velocity 25 cm/sec.) with a solution containing 45 parts by weight of amine, 40
60   parts by weight of sulfolane and 15 parts by weight
of water in a tray column with 30 trays at a pressure
of 80 bar and a temperature of 40°C, at such a space
velocity that the gas leaving the column contained
less than 4 ppmv of H_2S and 5 ppmv of CH_3SH. The
65   amines used were DEMEA and DIPA.

It was found that the required volume of the absorbent containing DIPA was 1.35 times larger than
that of the absorbent containing DEMEA (according
to the invention).

70   ### CLAIMS

1. A process for the removal of acid gases from a
gas mixture, characterized in that said gas mixture is
contacted at elevated pressure with an aqueous solution of a dialkyl - mono - alkanolamine, which
75   aqueous solution does not contain a sterically hindered amine.

2. A process as claimed in claim 1, characterized
in that the dialkyl - mono - alkanolamine used is
diethyl - mono - ethanolamine.

80   3. A process as claimed in claims 1 and 2, characterized in that at least 10% by weight of the aqueous
solution consists of dialkyl - mono - alkanolamine.

4. A process as claimed in claim 3, characterized
in that said percentage is between 15 and 60.

85   5. A process as claimed in any one of the preceding claims, characterized in that the pressure is at
least 5, preferably at least 10, bar.

6. A process as claimed in any one of the preceding claims, characterized in that the contacting
90   temperature is between 15 and 50°C.

7. A process as claimed in any one of the preceding claims, characterized in that the aqueous solution of a dialkyl - mono - alkanolamine also contains
a physical solvent for acid gases.

95   8. A process as claimed in claim 7, characterized
in that the physical solvent used is tetrahydrothiophene dioxide.

9. A process as claimed in claim 7 or 8, characterized in that the quantity of physical solvent is 10-40%
100 by weight of the aqueous solution.

10. A process as claimed in claim 1, substantially
as described with special reference to the Examples.